

and transport of the material. Also sensitivity determines to a large extent the governmental restrictions posed on transport and storage.

It is accordingly one object of the present invention to improve the stability of crystalline energetic materials. It is another object of the invention to improve the sensitivity, such as impact and friction sensitivity thereof.

These and other objects are realised by the present invention, which comprises a process for the production of crystalline energetic materials having improved stability and/or decreased sensitivity by crystallisation of the energetic materials with ultrasonic vibration having a frequency of between 10 and 100 kHz. Preferably the amplitude of an ultrasonic probe used for producing the vibration is between 0.4 and 30 μm .

The present invention is based on the surprising discovery, that by carrying out the last crystallisation step in the presence of ultrasonic vibration with a frequency of between 10 and 100 kHz, the morphology, stability and sensitivity can be improved, i.e. the crystals become more rounded, the stability is better and the sensitivity is less.

In US patent No. 3,222,231 published on December 7, 1965, it is disclosed to improve the morphology of crystalline material, including ammonium perchlorate and hydrazinium nitroformate, by precipitating a solid solute out of solution, while mechanically agitating the solution and subjecting it to a high frequency vibration. According to this patent, the processing under vibration improves the morphology of the crystals. The disclosure of this patent does not indicate anything about the effect of the treatment on stability and sensitivity.

According to a more preferred embodiment the present invention is directed to an improvement in the production of hydrazinium nitroformate (HNF). HNF belongs to the class

of high energy oxidisers and can be used in high performance chlorine free solid propellants.

HNF is generally produced in crystalline form by combining hydrazine and nitroform under well defined conditions, followed by further purification using i.a. crystallisation. One method for the production of HNF is described in US patent number 5,557,015. According to this method HNF is prepared in very pure form by reacting hydrazine and nitroform in a system that is a solvent for nitroform and a non-solvent for hydrazinium nitroformate, in the presence of a proton transferring medium.

The stability of the present energetic materials, and more in particular of HNF, can be determined by vacuum thermal stability (VTS) in accordance with STANAG 4479 at 60 and 80°C for 48 to 100 hours.

The friction sensitivity is determined by BAM friction in accordance with ONU 3b)i), the impact sensitivity by BAM impact in accordance with ONU 3a)ii).

It has been noted that whereas the HNF crystals are having an aspect ratio of more than 4 after crystallisation without ultrasonic vibration, the crystals produced in accordance with the process of the present invention have an aspect ratio, which is sometimes lower than this, depending both on the applied amplitude of the ultrasonic probe and the recrystallisation method used. However, it has also been found that there is no direct link between the aspect ratio of the crystals on the one hand and the stability or sensitivity on the other hand.

The process of the present invention can be carried out in various ways. In general it is important that during crystallisation the crystallising mixture is subjected to treatment with the ultrasonic vibration. This process can be applied during crystallisation and during recrystallisation.

In case of batch processing one may subject the whole batch at the same time to an ultrasonic vibration. In

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EXAMPLE 1 (ultrasound (US) applied during cooling-crystallisation of HNF)

5 Nitroform, dissolved in dichloroethane (23 wt.% nitroform), and water (6 vol.%) are mixed. At 0°C an equimolar amount of hydrazine, purity 99.5%, is added and the mixture is stirred, while keeping the temperature between 0 and 5°C. The crystalline HNF obtained thereby is
10 separated from the mother liquor and redissolved in methanol.

The HNF solution in methanol is subsequently cooled yielding HNF crystals. This experiment has been performed in the absence of ultrasound (US) (reference, amplitude
15 0 μm) and under ultrasonic vibration with a frequency of 20 kHz and varying ultrasonic amplitude. Figures 1, 2, 3 and 4 show the properties of HNF crystals obtained in several experiments in which the amplitude of ultrasonic vibration is varied during cooling crystallisation.

20 Figure 1 shows the positive effect of ultrasound (US) on the morphology of HNF, expressed as the Length over Diameter (L/D) and average particle size ($X_{\text{sph.}}$).

Figure 2 shows the positive effect of ultrasound (US) on the sensitivity of HNF, expressed in BAM impact and
25 BAM friction values ([N] and [N.m] respectively).

Figure 3 shows that ultrasound (US) has a positive effect on the thermal stability of HNF at 60°C. The initial gas evolution decreases in comparison to the reference sample (no ultrasound (US) = amplitude of 0 μm) and the gas
30 evolution in time decreases as well when a low amplitude of 0.4 μm is applied.

Figure 4 gives an indication of the positive effect of ultrasound (US) on thermal stability at 80°C. At 80°C the effect becomes more apparent (on the larger gas
35 evolution scale) after -80 hrs. These four figures clearly show the positive effect of ultrasound (US) during cooling

crystallisation on morphology, sensitivity and stability in comparison to the reference HNF crystallised in absence of ultrasound (US).

5 **EXAMPLE 2 (ultrasound (US) applied during drowning out crystallisation of HNF)**

HNF is prepared by the method described in example 1. The HNF in methanol solution is subsequently closed in a methylene chloride/methanol solution yielding HNF crystals. This experiment has been performed in the absence of ultrasound (US) (reference, amplitude 0 μm) and under ultrasonic vibration with a frequency of 20 kHz and varying ultrasonic amplitude. Figures 5, 6 and 7 show the properties of HNF crystals obtained in several experiments in which the amplitude of ultrasonic vibration is varied during drowning out crystallisation.

Figure 5 shows the negative effect of ultrasound (US) on morphology; L/D increases which implies that the HNF crystals are more needle shaped.

Figures 6 and 7 show VTS results at 60 and 80°C, respectively.

From figure 6 it can be clearly seen that ultrasound (US) application reduces initial gas evolution with a minimum initial gas evolution at a low to medium ultrasound (US) amplitude (0.4-2 μm).

Figure 7 shows that at higher temperature (80°C) the application of ultrasound (US) not only reduces the initial gas evolution but also the overall gas evolution rate in time. These three figures clearly show that in spite of the negative influence of ultrasound (US) during drowning-out crystallisation on morphology, ultrasound (US) has a positive influence on stability in comparison to the reference HNF crystallised in absence of ultrasound (US).